

PATENT SPECIFICATION

(11)

1 398 422

1 398 422

- (21) Application No. 785/75 (22) Filed 21 June 1972
 (62) Divided Out of No. 1 398 421
 (31) Convention Application No. 156 933 (32) Filed 25 June 1971 in
 (33) United States of America (US)
 (44) Complete Specification published 18 June 1975
 (51) INT CL² C11D 1/28, 3/33, 3/34
 (52) Index at acceptance
 C5D 6A5E 6B12A 6B12B1 6B12B2 6B12B3 6B12G2A
 6B12G3 6B12G4 6B12G6 6B12N1 6B1 6B2 6C6
 (72) Inventor VINCENT LAMBERTI



(54) SULFOSUCCINATE DERIVATIVES AS DETERGENT BUILDERS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Eutrophication is the process of excessive fertilisation of aquatic plants through enrichment of waters with nutrients, such as carbon, nitrogen, phosphorous, potassium, iron, trace metals and vitamins.

Although there is no present adequate proof, it has been postulated that the phosphorus-containing builders present in detergent compositions can be a factor in eutrophication. Therefore any substitutes which do not contain phosphorus may decrease to some extent the eutrophication.

It is an object of the present invention to provide detergent compositions which are free of phosphorus-containing builders such as the alkali metal condensed phosphates.

It has now been discovered that the alkali metal, ammonium and substituted ammonium salts of α -substituted - β -sulfosuccinic acids can serve as effective detergent builders in detergent compositions.

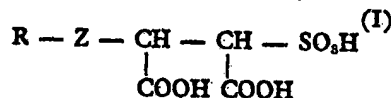
Accordingly, the present invention provides a detergent composition comprising:

- (a) at least one anionic, nonionic, zwitterionic or ampholytic detergent surface active agent; and
- (b) an organic detergent builder which is an alkali metal, ammonium or substituted ammonium salt of an α -substituted - β -sulfosuccinic acid wherein said builder represents from 5% to 90% of the total weight of the detergent composition.

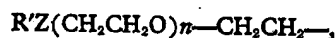
Many of the detergent builders and their

[Price 33p]

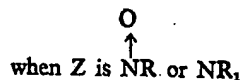
acid forms are novel and are claimed in the specification of the patent application No. 29057/72 (Serial No. 1,398,421). These novel compounds are the α -substituted - β -sulfosuccinic acids and alkali metal, ammonium or substituted ammonium salts thereof, having the general formula:



wherein Z is O, S, SO, SO₂, NR or NR₁, (wherein R₁ is hydrogen or R); R is C₁—C₃₀ alkyl, (C₁—C₃₀) hydroxyalkyl or (C₂—C₂₀) alkoxyalkyl, phenyl, carboxyl substituted or mono-, di- or tri-alkyl substituted phenyl, wherein each of the alkyl group or groups contain 1 to 4 carbon atoms; sulfo-alkyl or carboxy-alkyl, wherein the alkyl moieties contain 1 to 4 carbon atoms; or



wherein R' is H or alkyl containing 1 to 24 carbon atoms; and n is O or an integer of from 1 to 15, and when



the group R may be joined with the nitrogen atom to form a morpholinyl group, and when Z is O and the group R is an alkyl group the latter contains 2 to 30 carbon atoms.

Thus, specific compounds and classes of compounds embraced by the generic formula above include:

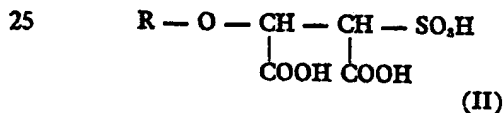
- α -alkoxy- β -sulfosuccinic acids
- α -phenoxy- β -sulfosuccinic acids

Best Available Copy

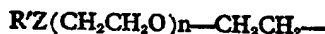
α -carboxyphenoxy- β -sulfosuccinic acids
 α -alkylphenoxy- β -sulfosuccinic acids
 α -carboxyalkoxy- β -sulfosuccinic acids
 α -sulfoalkoxy- β -sulfosuccinic acids
 α -alkoxyethoxy- β -sulfosuccinic acids
 α -alkoxypolyethyleneoxyethoxy- β -sulfo-
 succinic acids
 α -hydroxyalkoxy- β -sulfosuccinic acids;

the alkali metal, ammonium and substituted
 ammonium salts thereof; and the thio, sulfinyl
 and sulfonyl analogs of all the foregoing com-
 pounds wherein the oxygen group attached to
 the α -carbon of the succinic acid or succin-
 ate moiety is replaced by $-\text{S}-$, $-\text{SO}-$ or
 $-\text{SO}_2-$, respectively, and/or wherein the
 cases of the α -alkoxyethoxy compounds and
 the α -alkoxypolyethyleneoxyethoxy compounds
 the oxygen attached to the alkyl group (R')
 is replaced by $-\text{S}-$, $-\text{SO}-$ or $-\text{SO}_2-$.

Thus, the detergency builder compounds of
 the present invention include the compounds
 of Formula I above. Referring to Formula I
 above when Z is O, the detergency builders
 have the general formula:

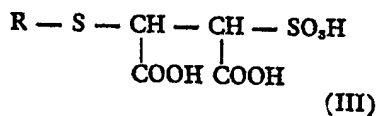


wherein R is hydrogen; alkyl or hydroxyalkyl
 or alkoxyalkyl containing 1—30 carbon atoms;
 phenyl; carboxy substituted or mono-, di- or
 tri-alkyl substituted phenyl wherein the alkyl
 groups each contain 1—4 carbon atoms; sulfo-
 or carboxy-alkyl wherein the alkyl moiety con-
 tains 1—4 carbon atoms; or

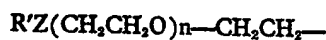


(wherein R' is hydrogen or alkyl containing
 1—24 carbon atoms, n is O or an integer of
 1—15 and Z is O, S, SO or SO_2); or
 mixtures thereof. Preferably R is a (C_1 — C_{24})
 alkyl, hydroxy (C_1 — C_{24}) alkyl or (C_1 — C_{24})
 alkoxy ethyl group.

When Z is S, the detergency builder com-
 pounds have the formula:

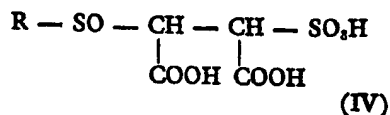


wherein R is hydrogen; alkyl containing 1—30
 (preferably 1—24) carbon atoms (e.g. C_{10} ,
 C_{16} , C_{18}); phenyl; carboxy substituted or
 mono-, di- or tri-alkyl substituted phenyl
 wherein the alkyl group or groups contain
 1—4 carbon atoms; sulfo- or carboxy-alkyl
 wherein the alkyl moieties each contain 1—4
 carbon atoms; or

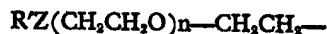


(wherein R' is H or alkyl containing 1—24
 carbon atoms, n is O or an integer of from
 1—15 and Z is O, S, SO or SO_2).

When Z is SO_2 , the detergency builder com-
 pounds have the formula:

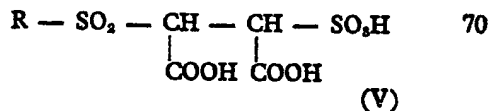


wherein R is alkyl containing 1—30 carbon
 atoms; phenyl; carboxy substituted or mono-,
 di- or tri-alkyl substituted phenyl wherein the
 alkyl group or groups contain 1—4 carbon
 atoms; sulfo- or carboxy-alkyl wherein the
 alkyl moiety contains 1—4 carbon atoms; or

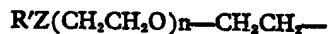


(wherein R' is H or alkyl containing 1—24
 carbon atoms, n is O or an integer of from
 1—15 and Z is O, S, SO or SO_2).

And when Z is SO_2 , the detergency builder
 compounds have the formula:

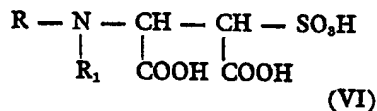


wherein R is alkyl containing 1—30 carbon
 atoms; phenyl; carboxy substituted or mono-,
 di- or tri-alkyl substituted phenyl wherein
 the alkyl group or groups contain 1—4 carbon
 atoms; sulfo- or carboxy-alkyl wherein the
 alkyl moiety contains 1—4 carbon atoms; or



(wherein R' is H or alkyl containing 1—24
 carbon atoms, n is O or an integer of from
 1—15 and Z is O, S, SO or SO_2).

Further detergency builder compounds
 according to the present invention are the
 nitrogen containing α -substituted- β -sulfo-
 succinic acids and the alkali metal, ammonium
 and substituted ammonium salts thereof having
 the following general formula:



wherein the groups R and R_1 may be the
 same or different and are C_1 to C_{20} alkyl,
 C_1 to C_4 hydroxyalkyl, carboxymethyl, carbo-
 oxyethyl, sulfomethyl and sulfoethyl, or one
 but not both of R and R_1 may be hydrogen or
 R and R_1 may be joined with the N-atom
 to form a morpholinyl moiety.

Representative compounds and classes of
 compounds embraced by generic Formula VI
 above include:

α - alkylamino - β - sulfosuccinic acids such as α -methylamino, α -propylamino, α -octylamino and α - laurylamino - β - sulfosuccinic acid;

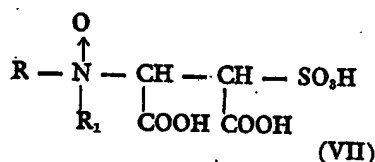
5 α - dialkylamino - β - sulfosuccinic acids such as α -dimethylamino, α -ethylmethylamino, α -methylhexylamino and α -dioctylamino - β -sulfosuccinic acid;

10 α - hydroxyalkyl - β - sulfosuccinic acids such as α - hydroxyethylamino, α -hydroxybutylamino and α -bis (hydroxyethyl) amino- β -sulfosuccinic acid;

15 α - carboxyalkylamino - β - sulfosuccinic acids such as α -carboxymethylamino, α -carboxyethylamino - β - sulfosuccinic acid and the corresponding sulfo analogs;

α - morpholinyl - β - sulfosuccinic acid; and the mono or poly salts thereof.

20 In accordance with a further specific aspect of the present invention are the amine oxide derivatives of Formula (VI), wherein the nitrogen is a tertiary atom, corresponding to the following general formula:



25 wherein R and R₁ are as is designated in Formula (VI) with the proviso that neither R or R₁ can be hydrogen.

30 As will be appreciated by those skilled in the art, the compounds of the invention contain at least two asymmetric carbon atoms and therefore can exist in several optically active forms as well as optically inactive mixtures (racemates). For purposes of this invention, the compounds as defined are intended to include all of the stereoisomeric forms and mixtures thereof.

35 In addition to the detergent building properties exhibited by the entire class of compounds described above, certain select members also exhibit properties which make them useful as wetting and foaming agents and thus constitute a class of novel surface active agents. For example, the α - alkoxy - β - sulfosuccinic acids and the thio analogs, containing 40 1—8 carbons, preferably from 1 to 4 carbon atoms, exhibit excellent detergent building properties whereas the higher homologs containing 9—30 and more preferably 9—24 carbon atoms in the alkyl chain (for example the α -dodecyloxy, hexadecyloxy, octadecyloxy and tetradecyloxy - β - sulphosuccinate) additionally exhibit wetting, foaming and detergency properties.

50 Similarly, the α -alkoxyethoxy and α -alkoxy-polyethyleneoxyethoxy - β - sulfosuccinic acid compounds containing from about 9—30 and preferably about 9—24 carbon atoms in the alkoxy moiety are also useful as wetting agents,

foaming agents and detergents as well as detergent builders.

60 Although the builders of the present invention may be utilized as the free acid provided sufficient alkaline additives are included in the detergent composition to convert the acid forms in situ to the normal salt forms, the alkali metal, ammonium and substituted ammonium salts of the α - substituted - β - sulfosuccinic acids are preferred. Included in the substituted ammonium salts that can be employed are the monoethanolammonium, diethanolammonium, triethanolammonium, methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, morpholinium, N - methylmonoethanolammonium and N-ethylmonoethanolammonium salts and mixtures thereof.

70 The utility of the compounds of the present invention is not only reflected in terms of excellent building and biodegradability properties but also in low cost of preparation, since they are prepared from readily available and inexpensive materials. For example, the compounds of this invention are derived from sulfomaleic anhydride and readily available alcohols, thiols, hydroxy acids and amines.

80 More specifically, the compounds of this invention are reaction products derived by reaction between sulfomaleic acid and compounds having an active hydrogen atom.

85 Compounds having an active hydrogen and suitable for use in preparing the compounds of the present invention are mono-, di- or polyhydric alcohols and mono-, di- or polyhydroxy acids and their sulfur-containing analogs. Suitable examples of the aforementioned monohydric alcohols include alkoxyalkanols such as methoxyethanol and the linear primary and secondary alcohols containing up to 30 carbon atoms and their thio analogs; aromatic hydroxy compounds particularly the carbocyclic mono- and bicyclic aromatic hydroxy compounds, such as naphthols and phenols and the mono-, di or tri- C₁—C₄ alkyl ring substituted derivatives thereof. Suitable examples of dihydric alcohols include the glycols such as ethylene glycol, propylene glycol, butylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, heptamethylene glycol, long chain 1,2-diols containing from 8—30 carbon atoms and aromatic carbocyclic glycols such as phenylethylene glycol. Similarly, suitable polyhydric alcohols include glycerol, pentaerythritol, hexanetriol, sugars and their thio analogs.

100 In addition to the alcohols, the hydroxy carboxylic and sulfonic acids (in their ester and acid/salt forms, respectively) may also react with sulfomaleic anhydride and sulfomaleic acid. These include glycollic, lactic, 105 glyceric, hydroxypropionic, salicylic and mercapto acetic acid, hydroxymethanesulfonic acid and hydroxyethanesulfonic acid.

60

65

70

75

80

85

90

95

100

105

110

115

120

Still another important class of compounds containing active hydrogens are ethylene oxide adducts of C_1 to C_{30} primary and secondary alcohols with 1—15 moles of ethylene oxide.

5 In general, the α -substituted- β -sulfosuccinate salts, wherein the α -substituent is joined to the α -carbon atom of the sulfosuccinate moiety by an O or S linkage, may be prepared by heating at a temperature of
10 from about 25 to 120° C., preferably 60 to 100° C., sulfomaleic anhydride with a suitable compound having an active hydrogen atom as described above followed by further
15 treatment with a base for example an alkali metal hydroxide. The desired α -oxy or α -thio- β -sulfosuccinate may then be recovered and purified using conventional techniques.

20 The α -substituted- β -sulfosuccinate salts wherein the α -substituent is joined to the α -carbon atom of the sulfosuccinate moiety by an SO or SO_2 linkage may be prepared by treating the appropriate α -substituted thio- β -sulfosuccinate with hydrogen peroxide according to the methods described on pages 471—
25 472 in the text, "Reagents for Organic Synthesis" by Fieser and Fieser, published by John Wiley & Sons, Inc., 1967.

30 The α -substituted- β -sulfosuccinate salts wherein the α -substituent is joined to the α -carbon atom of the sulfosuccinate moiety by an amino function (as in Formula VI) may be prepared by reacting an appropriately substituted or unsubstituted primary or secondary amine with alkali metal salts of sulfomaleic acid. Typical amines suitable for reaction to form the α -substituted amino- β -sulfosuccinates include:

40 ethanolamine
diethanolamine
propanolamine
morpholine
N-methylethanolamine
glycine
alanine
45 N-methyl taurine
alkylamines containing 1—20 carbons in the alkyl chain, as well as other amines having a replaceable or active hydrogen and a basicity comparable to the
50 aforementioned amines.

55 In particular the α -amino substituted- β -sulfosuccinates derived from water-soluble amines may be prepared by reacting in aqueous solution without the aid of heat and those derived from water-insoluble amines (i.e., higher alkylamines) are reacted in a mixed solvent system such as ethanol/water or dioxane/water at temperatures ranging from about 25° C. to about 80° C.; isolation from the reaction medium, and purification if desired, being effected by conventional
60 methods.

The compounds wherein the α -substituent is

joined to the α -carbon atom by an amine oxide group, as in Formula (VII), may be prepared by reacting the tertiary amine compounds of Formula (VII) VI with oxidizing agents such as hydrogen peroxide, peroxyacetic and peroxyformic acid in the manner described for oxidizing tertiary amines by Hoh et al., J. Am. Oil Chemists' Soc., 40, 268 (1963). 65 70

In preparing the sulfosuccinate salts from the free acid, the amount of base utilized will determine whether the mono-, di- or tri-salt is obtained. For example, the use of one mole of base (i.e., sodium hydroxide) per mole of α -hydroxy- β -sulfosuccinic acid yields the monosodium salt; the use of two moles of sodium hydroxide, the disodium salt and the use of three moles of sodium hydroxide, the trisodium salt. When R is carboxymethyl, carboxyethyl, sulfomethyl or sulfoethyl, a tetrasalt can also be obtained. Similarly, other bases, such as ammonium hydroxide and organic amines, may be utilized in the same manner to afford the type of salt desired. 75 80 85

According to the present invention, excellent cleaning results can be obtained by using the detergency builders described above with a wide range of detergent surface active materials and mixtures thereof in any of the usual physical forms for such compositions such as powders, beads, flakes, bars, tablets, noodles, liquids and the like. The builders can be used singularly, in combination with each other as the sole builder in the detergent composition or in combination with other well-known detergent builders such as sodium nitrilotriacetate, sodium ethylenediaminetetraacetate, sodium tripolyphosphate, trisodium orthophosphate, sodium and potassium pyrophosphate, sodium polyacrylate, disodium oxydiacetate, trisodium citrate, trisodium carboxymethylxysuccinate, salts of oxidized starches and sodium or potassium carbonate, as well as other conventional organic and inorganic builders. 90 95 100 105

When using the detergent compositions of the invention to wash clothes, the wash solutions should have a pH from about 7 to 12 and preferably from 9 to 11 throughout the washing cycle. Therefore, the presence of an alkaline buffer in the detergent composition is usually desirable particularly when the soil to be removed from the clothes has a high content of acidic components. Suitable buffers include any of the common organic and/or inorganic buffers such as monoethanolamine, diethanolamine, triethanolamine, sodium and potassium silicates, sodium and potassium carbonates and bicarbonates and the like. 110 115 120

In the detergent compositions of the present invention, the only essential ingredients are the detergent surface active material and the builder. The weight percent of the builder present in the detergent composition will range from 5 to 90% and preferably from 20 to 125

60% and more preferably 35—50% by weight of the total weight of the composition. When expressed as a weight ratio of builder to surfactant, the builders used in the instant invention will generally be present in a ratio of 1:10 to 10:1, and preferably 2:1 to 5:1 depending on the end use of whether a heavy-duty or light-duty detergent is desired. When the builders are used in mechanical dish-washing compositions, the ratio of builder to surfactant is from about 10:1 to about 50:1.

The detergent surface active compounds which can be used within the compositions of this invention include anionic, nonionic, zwitterionic, ampholytic detergent compounds and mixtures thereof. These suitable substances are outlined at length below.

(a) Anionic detergent compositions which can be used in the compositions of this invention include both soap and non-soap detergent compounds. Examples of suitable soaps are the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids (C_{10} — C_{18}). Particularly useful are the sodium or potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap and tall oil. Examples of anionic organic non-soap detergent compounds are the water soluble salts, alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of the synthetic detergents which form a part of the compositions of the present invention are the sodium or potassium alkyl sulfates especially those obtained by sulfating the higher alcohols (C_8 — C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzenesulfonates in which the alkyl group contains from about 9 to about 20 carbon atoms and in which the alkyl group is attached to the benzene ring in either the one position or at the secondary positions such as in sodium linear secondary alkyl (C_{10} — C_{18}) benzene sulfonate (commonly abbreviated to LAS), sodium p-(2-dodecyl)benzenesulfonate, sodium p-(2-octadecyl)benzenesulfonates and sodium p-(3-dodecyl)benzenesulfonate; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters and carboxymethylated derivatives of the reaction product of one mole of a higher derived from petroleum; sodium coconut oil alcohols) and about 1 to 6 moles of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to about 18 carbon

atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl taurine in which the fatty acids, for example, are derived from coconut; alkane sulfonates such as those derived by reacting alpha-olefins containing 8 to 20 carbon atoms with sodium bisulfite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulfonate; alpha-olefin sulfonates such as those derived by reacting alpha-olefins with SO_2 and then neutralizing the reaction product; and others known in the art.

(b) Nonionic synthetic detergents may be broadly defined as compounds which do not ionize in water solution. For example, a well-known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic" (Registered Trade Mark). These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1,500 to 1,800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkylphenols, e.g., the condensation products of alkylphenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkylphenols. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, dodecene, or nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said hydrophobic base having a molecular weight of the order of 2,500 to 3,000 are satisfactory.

(3) The condensation product of aliphatic alcohols, primary or secondary, having from

- 8 to 18 carbon atoms, in either straight chain or branched configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 6 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms; a $C_{11}-C_{15}$ random secondary alcohol derived from n-paraffins and condensed with 7 moles of ethylene oxide per mole of secondary alcohol.

(4) Long chain tertiary amine oxides corresponding to the following general formula,



- wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms and R_2 and R_3 are each methyl, ethyl or hydroxy ethyl radicals. The arrow in the formula is a conventional representation of semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyloctylamine oxide, dimethyldodecylamine oxide, dimethyltetradecylamine oxide and dimethylhexadecylamine oxide and N-bis-(hydroxyethyl)dodecylamine oxide.

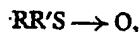
- (5) Long chain tertiary phosphine oxides corresponding to the following formula



- wherein R is an alkyl, alkenyl or monohydroxy-alkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are:

- dimethyldodecylphosphine oxide,
dimethyltetradecylphosphine oxide,
ethylmethyltetradecylphosphine oxide,
cetyl-dimethylphosphine oxide,
dimethylstearylphosphine oxide,
cetyl-ethylpropylphosphine oxide,
diethyldodecylphosphine oxide,
diethyltetradecylphosphine oxide,
bis (hydroxymethyl) dodecylphosphine oxide,
bis (2-hydroxyethyl) dodecylphosphine oxide,
2 - hydroxypropylmethyltetradecylphosphine oxide,
dimethylolelylphosphine oxide, and
dimethyl-2-hydroxydodecylphosphine oxide.

- (6) Dialkyl sulfoxides corresponding to the following formula,



- wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the R groups ranging from 10 to 18

carbon atoms in chain length, and wherein R' is methyl, ethyl or alkylol. Examples of suitable sulfoxide compounds are:

- dodecyl methyl sulfoxide
tetradecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
2-hydroxydodecyl methyl sulfoxide
3-hydroxy-4-decyloxybutyl methyl sulfoxide
3-hydroxy-4-dodecyloxybutyl methyl sulfoxide
2-hydroxy-3-decyloxypropyl methyl sulfoxide
2-hydroxy-3-dodecyloxypropyl methyl sulfoxide
dodecyl ethyl sulfoxide
2-hydroxydodecyl ethyl sulfoxide
dodecyl-2-hydroxy ethyl sulfoxide

(c) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds falling within this definition are sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropanesulfonate and sodium N-2 - hydroxydodecyl - N - methyl - taurate.

(d) Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium compounds, sulfonium compounds and phosphonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds falling within this definition are 3 - (N,N - dimethyl - N - hexadecylammonio)-propane - 1 - sulfonate, 3 - (N,N - dimethyl - N - hexadecylammonio - 2 - hydroxy - propane - 1 - sulfonate, 3 - (dodecylmethyl-sulfonium) propane sulfonate, and 3 - (cetyl-methylphosphonium)ethane sulfonate.

Other materials which may be present in the detergent compositions of the invention in generally minor amounts are those conventionally present therein. Typical examples thereof include the well-known soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers such as sodium sulfate, optical brighteners, perborates, bleaches, bleach activators, enzymes, suds boosters, suds depressants, germicides, fungicides, anti-tarnishing agents, cationic detergents, fabric softening agents and in the case of liquid compositions, opacifiers and organic solvents. The balance of the detergent compositions may be water or inert filler.

It has been discovered that when higher than normal levels of anionic, nonionic, ampholytic or zwitterionic surfactants are used with the sulfosuccinate derivative salts of this invention, the detergency of the formu-

lation is significantly enhanced particularly at low formulation concentrations ($\sim 0.1\%$) which are typically used by the housewife. For enhanced results the detergent formulation should contain surfactant levels of about 25% to about 45% by weight and the sulfosuccinate derivative salt levels of about 25% to about 75% by weight in the cases where the surfactants are anionic, ampholytic or zwitterionic. When the surfactant is a nonionic, enhanced detergency results are obtained when the level of said nonionic in the formulation is from about 15% to 30% by weight and the level of sulfosuccinate derivative salt is from about 25% to about 85% by weight.

In addition to their use in general household detergent compositions, the builders of the present invention find utility as boiler scale removers, stain removers and general chelating agents. When used at pH's of about 2 to about 5 as partially neutralized alkali metal, ammonium or substituted ammonium salts, especially in combination with wetting agents and surfactants, the compounds of the invention are excellent metal cleaning compounds.

Example I.

Table 1 below illustrates detergent compositions containing the detergency builders of the present invention in combination with representative classes of surface active agents compared with control or standard phosphate built detergent compositions. The compositions were prepared by blending together the recited components in the proportions indicated, including an anticorrosive agent and buffer agent (sodium silicate) and the balance being water. The compositions were then tested on vacuum cleaner dust soiled cloth for detergency or cleaning ability in the Terg-O-Tometer test; wherein washing conditions are as indicated and the results reported as detergency units. The average detergency units (DU) of the formulation is the final reflectance value of the washed cloth (average of 2 runs) minus the initial reflectance of the soiled cloth, the reflectances being obtained by measurement with a Gardner automatic color difference meter, Model AC-3.

TABLE I

Component	% Composition										Controls (% Composition)									
	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
α -hydroxy ^a																				
α -(2-hydroxy-ethoxy) ^a																				
α -dodecyloxy ^a																				
α -methoxy ^a																				
α -carboxymethoxy ^a																				
α -dodecyloxyethoxy ^a																				
α -dodecylthio ^a																				
$\text{Na}_3\text{P}_3\text{O}_{10}$																				
Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}=2.4:1$)																				
Anionic ^b																				
Anionic ^c																				
Nonionic ^d																				
Ampholytic ^e																				
Zwitterionic ^f																				
Water																				
Formulation Concentration, %	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Detergency (DU's)	24.6	24.4	26.5	23.1	25.6	26.1	24.7	27.1	23.0	24.2	15.4	22.3	4.8	6.4	16.1	19.9	18.8	20.1	28.7	29.4

balance

- *Sodium salts of α - substituted - β - sulfosuccinate
- *Sodium linear secondary alkyl (C_{10} — C_{18}) benzene sulfonate
5. *Sodium C_{15} — C_{18} α -olefin sulfonate
- * C_{11} — C_{15} linear secondary alcohols ethoxylated with 7 moles ethylene/oxide/mole alcohol
10. * C_{14} — C_{16} HAMT (sodium hydroxyalkyl N-methyl taurate)
- *Sulfobetaine DCH (cocodimethylsulfopropyl betaine)
- Washing conditions — 180 ppm (2:1 Ca^{++} /Mg $^{++}$); 120°F: pH 10
15. The preparation of specific α - substituted - β - sulphosuccinates is described in detail in Examples 2—11 of the parent specification 29057/72 (Serial No. 1,398,421).
- In addition Table 2 in the parent specification indicates the reactants required to obtain other α - substituent - β - sulfosuccinate detergency builder salts having the R and Z moieties set forth in Formula I, following the procedures of the appropriate examples, which detergency builder salts can be employed in compositions of the invention.
25. WHAT WE CLAIM IS:—
1. A detergent composition comprising:
30. (a) at least one anionic, nonionic, zwitterionic or ampholytic detergent surface active agent; and
- (b) an organic detergent builder which is an alkali metal, ammonium or substituted ammonium salt of an α - substituted - β - sulfosuccinic acid wherein said builder represents from 5% to 90% of the total weight of the detergent composition.
35. 2. A detergent composition according to claim 1, wherein the builder is a salt of an α - substituted - β - sulfosuccinic acid having the general formula:
- $$R - O - \underset{\substack{| \\ \text{COOH}}}{\text{CH}} - \underset{\substack{| \\ \text{COOH}}}{\text{CH}} - \text{SO}_3\text{H} \quad (\text{II})$$
45. wherein R is hydrogen; alkyl or hydroxyalkyl or alkoxyalkyl containing 1—30 carbon atoms; phenyl; carboxy substituted or mono-, di- or tri-alkyl substituted phenyl wherein the alkyl groups each contain 1—4 carbon atoms; sulfo- or carboxy-alkyl wherein the alkyl moiety contains 1—4 carbon atoms; or
50. $R'Z(\text{CH}_2\text{CH}_2\text{O})_n - \text{CH}_2\text{CH}_2 -$
- (wherein R' is hydrogen or alkyl containing 1—24 carbon atoms, n is 0 or an integer of from 1—15 and Z is O, S, SO or SO_2).
55. 3. A detergent composition according to claim 2, wherein R is alkyl having 1—24 carbon atoms.
4. A detergent composition according to claim 2, wherein R is alkyl having 9—24 carbon atoms.
60. 5. A detergent composition according to claim 2, wherein R is alkyl having 1—8 carbon atoms.
6. A detergent composition according to claim 2, wherein the builder is α - dodecyloxy - β - sulfosuccinate.
65. 7. A detergent composition according to claim 2, wherein the builder is α - hexadecyloxy - β - sulfosuccinate.
70. 8. A detergent composition according to claim 2, wherein the builder is α - octadecyloxy - β - sulfosuccinate.
9. A detergent composition according to claim 2, wherein the builder is α - tetradecyloxy - β - sulfosuccinate.
75. 10. A detergent composition according to claim 2, wherein R is hydroxyalkyl having 1—24 carbon atoms.
80. 11. A detergent composition according to claim 2, wherein the builder is α - hydroxyethoxy - β - sulfosuccinate.
12. A detergent composition according to claim 2, wherein the builder is α - hydroxy - β - sulfosuccinate.
85. 13. A detergent composition according to claim 2, wherein R is alkoxy (1—24 carbon atoms) ethyl.
14. A detergent composition according to claim 2, wherein the builder is α - dodecyloxyethoxy - β - sulfosuccinate.
90. 15. A detergent composition according to claim 2, wherein the builder is α - carboxymethoxy - β - sulfosuccinate.
95. 16. A detergent composition according to claim 1, wherein the builder is a salt of an α - substituted - β - sulfosuccinic acid having the general formula:
- $$R - S - \underset{\substack{| \\ \text{COOH}}}{\text{CH}} - \underset{\substack{| \\ \text{COOH}}}{\text{CH}} - \text{SO}_3\text{H} \quad (\text{III})$$
100. wherein R is hydrogen; alkyl containing 1—30 carbon atoms; phenyl; carboxy substituted or mono-, di- or tri-alkyl substituted phenyl wherein the alkyl group or groups contain 1—4 carbon atoms; sulfo- or carboxy-alkyl wherein the alkyl moieties each contain 1—4 carbon atoms; or
105. $R'Z(\text{CH}_2\text{CH}_2\text{O})_n - \text{CH}_2\text{CH}_2 -$
- (wherein R' is H or alkyl containing 1—24 carbon atoms, n is 0 or an integer of from 1—15 and Z is O, S, SO or SO_2).
110. 17. A detergent composition according to claim 16, wherein R is an alkyl group having 1—24 carbon atoms.
18. A detergent composition according to

claim 16, wherein R is an alkyl group having 1—8 carbon atoms.

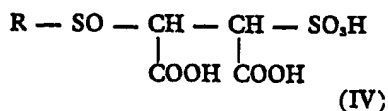
19. A detergent composition according to claim 16, wherein R is an alkyl group having 9—24 carbon atoms.

20. A detergent composition according to claim 16, wherein the builder is an α - dodecylthio - β - sulfosuccinate.

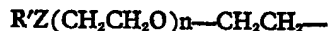
21. A detergent composition according to claim 16, wherein the builder is an α - hexadecylthio - β - sulfosuccinate.

22. A detergent composition according to claim 16, wherein the builder is an α - octadecylthio - β - sulfosuccinate.

23. A detergent composition according to claim 16, wherein the builder is a salt of an α - substituted - β - sulfosuccinic acid having the general formula:

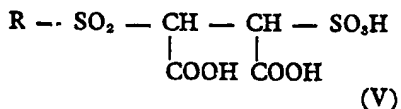


24. wherein R is alkyl containing 1—30 carbon atoms; phenyl; carboxy substituted or mono-, di- or tri-alkyl substituted phenyl wherein the alkyl group or groups contain 1—4 carbon atoms; sulfo- or carboxy-alkyl wherein the alkyl moiety contains 1—4 carbon atoms; or

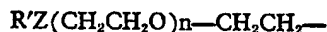


(wherein R' is H or alkyl containing 1—24 carbon atoms, n is O or an integer of from 1—15 and Z is O, S, SO or SO₂).

25. A detergent composition according to claim 1, wherein the builder is a salt of an α - substituted - β - sulfosuccinic acid having the general formula:



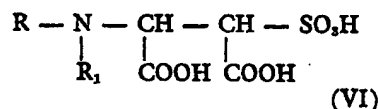
26. wherein R is alkyl containing 1—30 carbon atoms; phenyl; carboxyl substituted or mono-, di- or tri-alkyl substituted phenyl wherein the alkyl group or groups contain 1—4 carbon atoms; sulfo- or carboxy-alkyl wherein the alkyl moiety contains 1—4 carbon atoms; or



(wherein R' is H or alkyl containing 1—24 carbon atoms, n is O or an integer of from

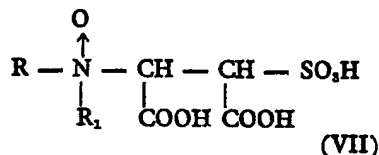
1—15 and Z is O, S, SO or SO₂).

27. A detergent composition according to claim 1, wherein the builder is a salt of an α - substituted - β - sulfosuccinic acid having the general formula:



wherein the groups R and R₁ may be the same or different and are C₁ to C₂₀ alkyl; C₁ to C₄ hydroxyalkyl; carboxymethyl; carboxyethyl; sulfomethyl; sulfoethyl; or one but not both of R and R₁ may be hydrogen, or R and R₁ may be joined with the N atom to form a morpholinyl moiety.

28. A detergent composition according to claim 1, wherein the builder is a salt of an α - substituted - β - sulfosuccinic acid having the general formula:



wherein R and R₁ are the same or different and are C₁ to C₂₀ alkyl, C₁ to C₄ hydroxyalkyl, carboxymethyl, carboxyethyl, sulfomethyl or sulfoethyl; or R and R₁ may be joined with the N atom to form a morpholinyl moiety.

29. A detergent composition according to any of the preceding claims wherein the detergent builder compound is a sodium salt.

30. A detergent composition according to any of the preceding claims comprising from about 20 to 60% by weight of the detergent builder.

31. A detergent composition according to any of the preceding claims, wherein the weight ratio of the builder to the detergent compounds is from 1:10 to 10:1.

32. A detergent composition according to claim 1 substantially as described herein with reference to any one of the Examples in Table 1.

R. V. TATE,
Chartered Patent Agent,
Unilever Limited,
Unilever House,
London, E.C.4.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☒ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.